PHOTOINDUCTIVE DEGRADATION OF TWO ESTROGENS BY NATURAL DISSOLVED ORGANIC MATTER UNDER SIMULATED SUNLIGHT

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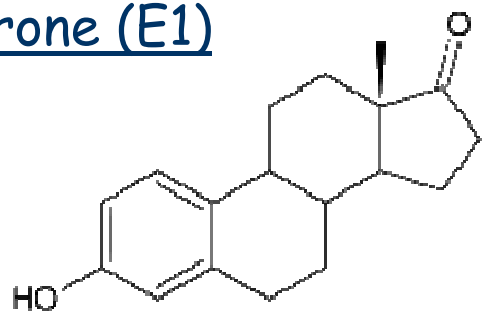
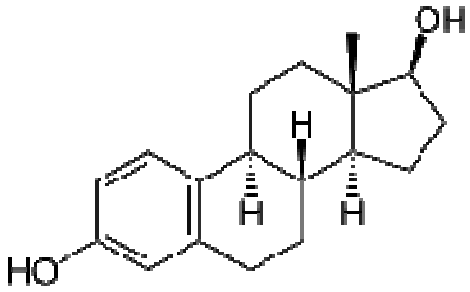
EMEC 10 Limoges 12/04/09

Introduction

Estrone (E1)



17ß-estradiol (E2)



- Presence in the environment

- natural estrogens (steroidal hormones) present in aquatic media (through animals excretion)

- released into surface and ground waters through wastewater effluents

- detected in soils adjacent to agricultural fiels fertilized with animals waste

- E1 and E2 = two main estrogens detected in fresh and marine waters ~ in ng/L, Hohenblum 2004, Zuo 2006)

Introduction

- Effects on aquatic organisms

  - impact on reproductive system and development of reproductive organs (Jobling 2002, Rodgers-Gray 2000)
  - estrogenic effects detected for vertebrates and invertebrates, fishes, amphibians, reptiles (feminisation, … Orlando 2004, Brion 2004, Lai 2002)

- Human impacts

  - increased incidents of breast, testicular and prostate cancer
  - reduced fertility of men (Harrison 1997, Colburn 1995, Carlsen 1995)

  - no conclusive relationships established between endocrine disruptor exposure and human health

- Photodegradation : half-lives under simulated solar system
  - E1 : 4,7 h (Lin et Reinhard 2005)
  - E2 : 13,6 h (Leech 2008)

Introduction

Natural Dissolved Organic Matter (DOM)

- Presence in the environment

  - complex matrix
  - natural decomposition of ecosystems : terrestrial and aquatic origins
  - composition and concentration depending on the nature and origin of the media (Thurman 1985)

- Photodegradation

  - degradation (break of aromatic structures Carvalho 2008)
  - light absorption and production of reactive species ($^1O_2$, OH°, RO°, solvated electrons, … Aguer 1999)

Materials and Methods

Photolysis

- Photodegradation under simulated sunlight (Suntest Atlas CPS+)

Suntest 8h, 250 W/m², 900 kJ/h :
- ~ 800 nM E1 or E2
- 20 mg/L DOM
- pH = 7

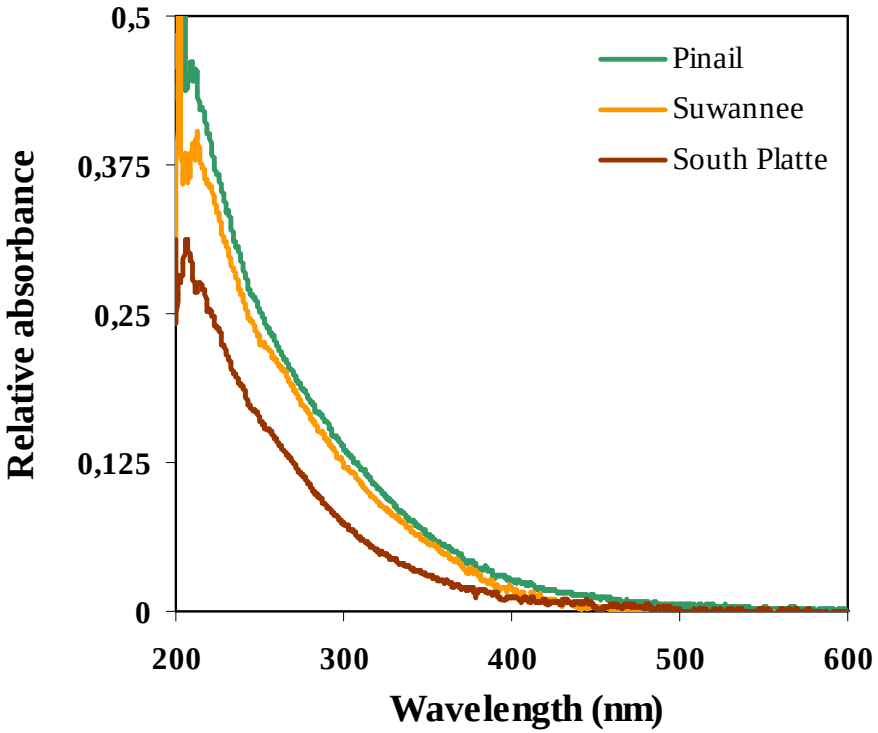
Analysis

- HPLC-UV
- Spectrophotometer, Fluorimeter, TOCmeter

Materials and Methods

Optical properties of DOM

➢ 3 extracts used in photolysis experiments :
fulvic acids of Pinail (France), Suwannee and South Platte (US rivers) at 20 mg DOM/L or 10 mg C/L



Order of UV-Visible absorbance

Pinail >

Suwannee >>

South Platte

Materials and Methods

Optical properties of DOM

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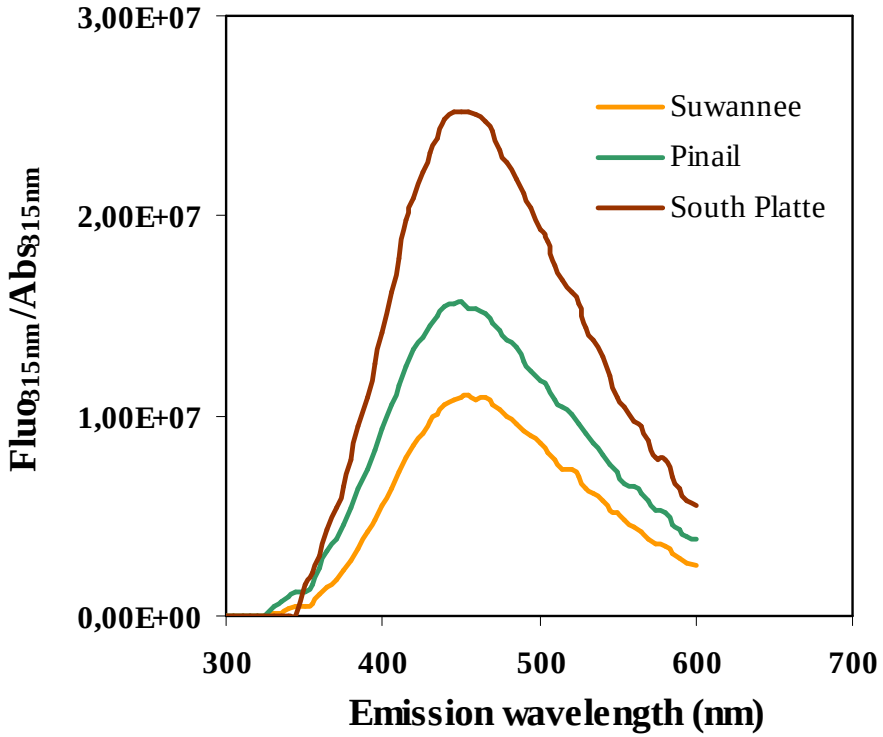


Fluorescence/Absorbance Order

South Platte > Pinail > Suwannee

South Platte

The most efficient

Indirect photolysis

Nature of DOM Influence → E1

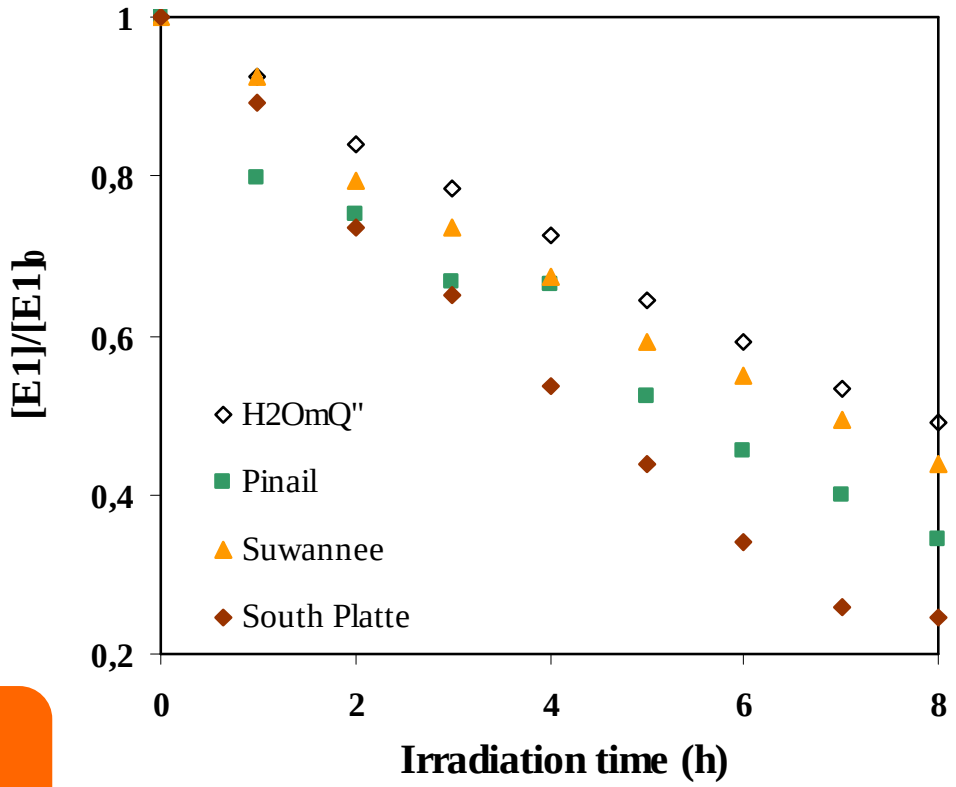
Photoinductive efficiency

South P. 76% >

Pinail 66% >

Suwannee 56%

Suntest 8h, 250 W/m², 800 nM E1, pH7



%Error (duplicates) : 2-5 %

Relationship between DOM nature – photoinductive efficiency

Indirect photolysis

Nature of DOM Influence → E2

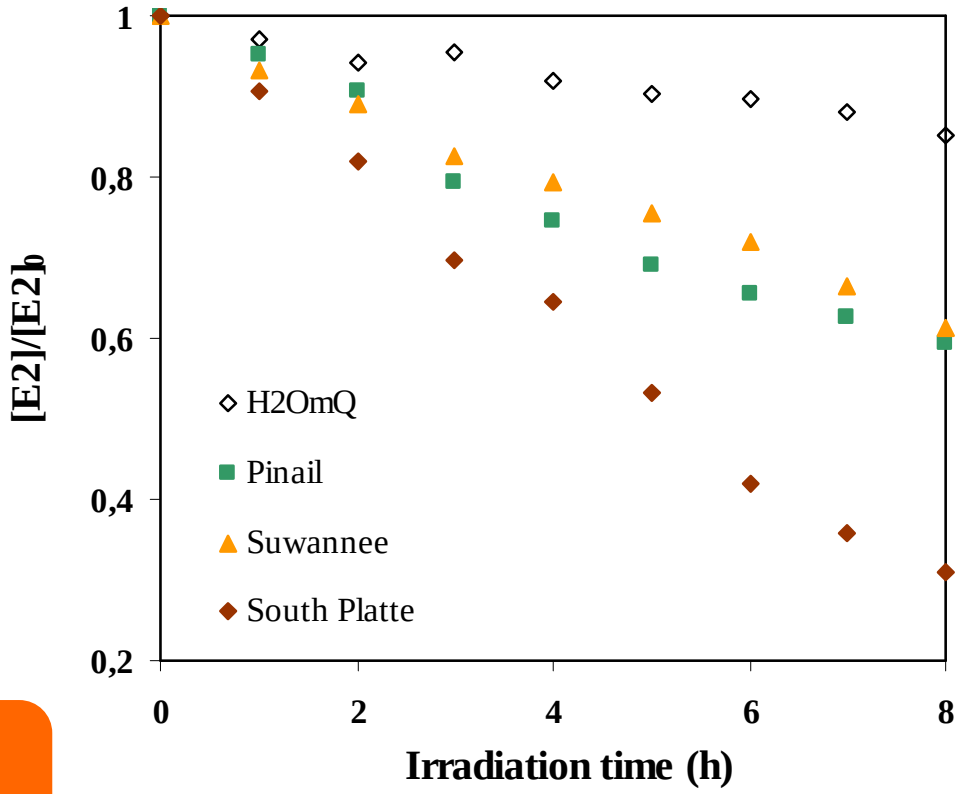
Photoinductive efficiency

South P. 69% >>

Pinail 41% >

Suwannee 39%

Suntest 8h, 250 W/m², 700 nM E2, pH7



%Error (duplicates) : 3-6 %

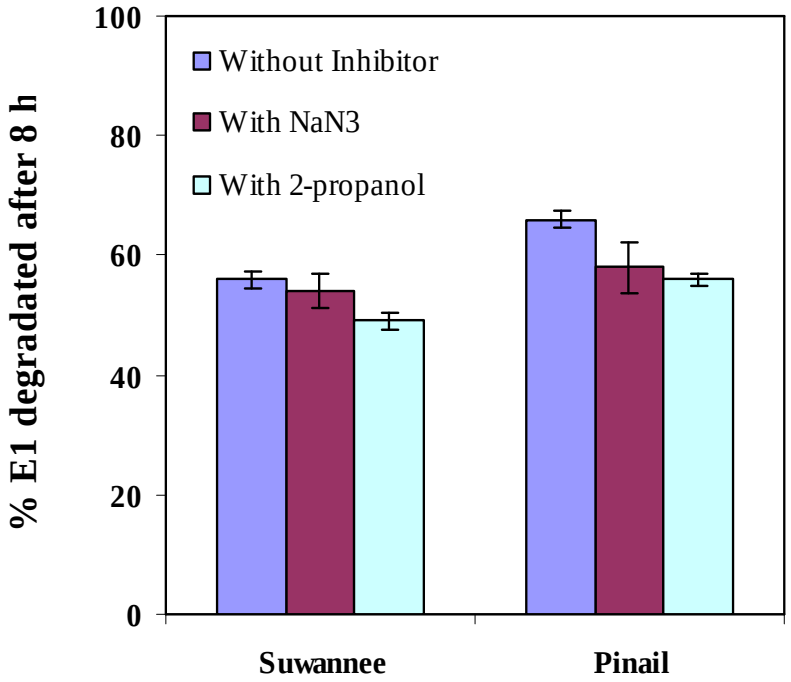
Relationship between DOM nature – photoinductive efficiency

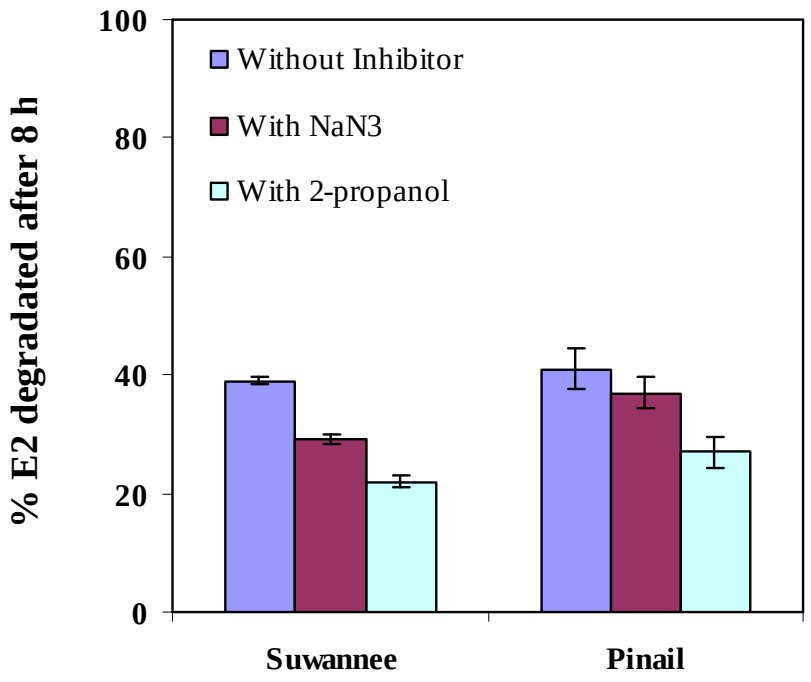
The more fluorescent the more photoinductive efficient

Indirect photolysis

Reactive species

- Addition of inhibitors : NaN_3 and 2-propanol





Photodegradation decrease with the addition of inhibitors

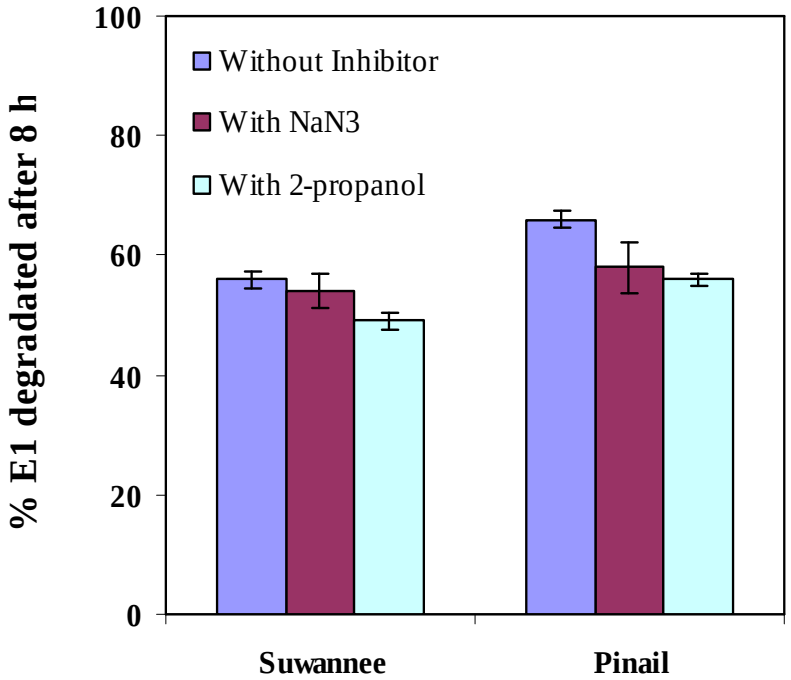
For every DOM :

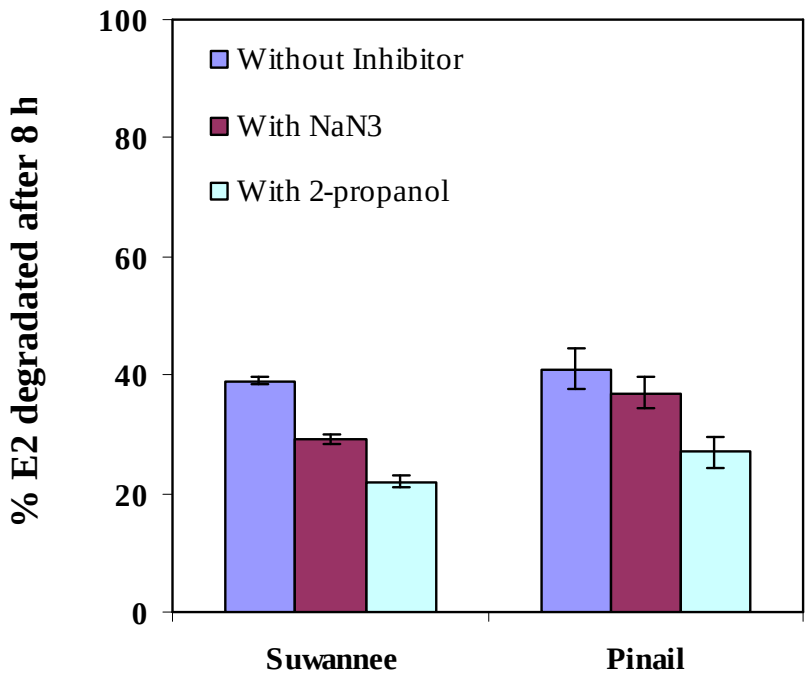
Degradation without inhibitor > with NaN3 > with 2-propanol

Indirect photolysis

Reactive species

- Addition of inhibitors : NaN_3 and 2-propanol





Reactive species in the inductive photodegradation

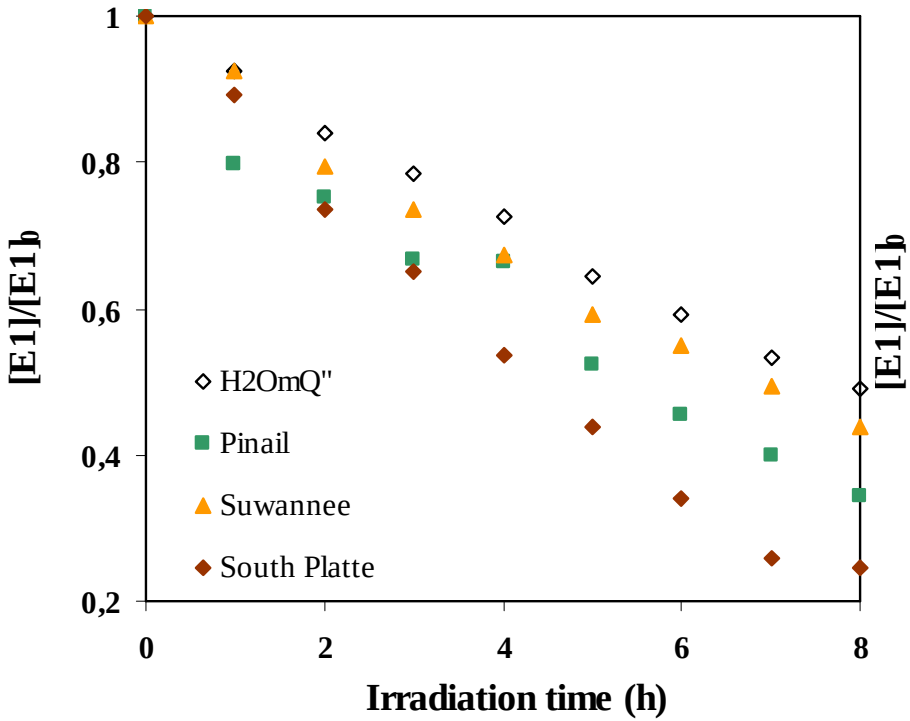
$^1O_2$: participation in the photodegradation about 2 – 10 %

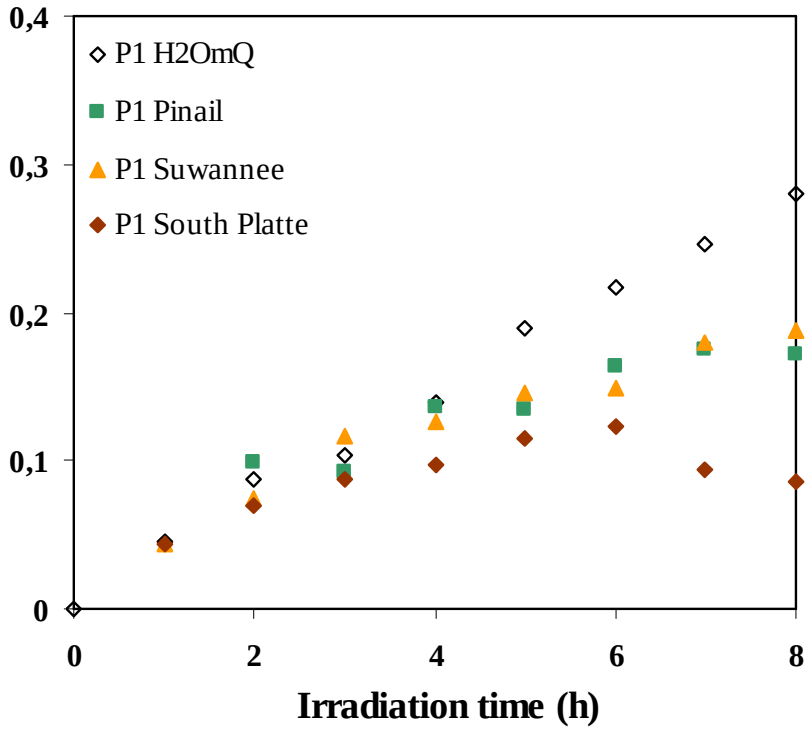
OH° : participation in the photodegradation about 7 – 1 7 %

Indirect photolysis

Photoproduct (P1)

- Formation kinetics





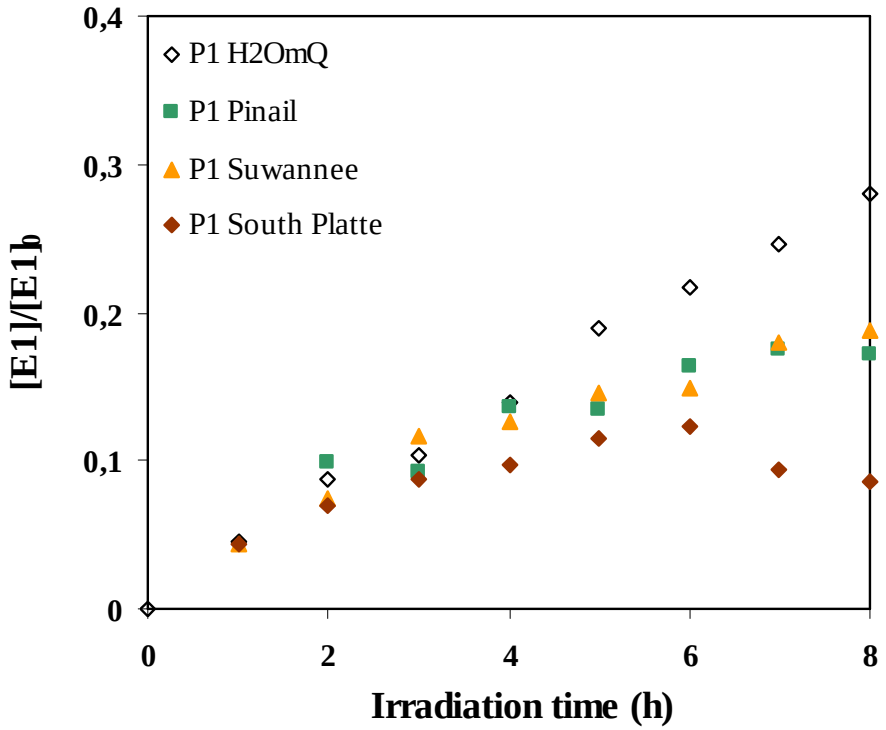
Indirect photolysis

Photoproduct (P1)

- Formation kinetics

P1 formation decreases in the presence of DOM

Degradation of P1 by S. P. after 6 h



P1 degradated by DOM

or

Optical filter effect of DOM

Indirect photolysis

Kinetics

➢ Pseudo-first order kinetic rate constants obtained for E1 and E2 during inductive photodegradation by DOM solutions

E1	k_{O2} (h^{-1})		$k_{O2+NaN3}$ (h^{-1})		k_{O2+Pro} (h^{-1})	
H_2OmQ	0,09	R^2=0,998				
Pinail	0,13	R^2=0,977	0,11	R^2=0,994	0,10	R^2=0,984
Suwannee	0,10	R^2=0,997	0,09	R^2=0,964	0,08	R^2=0,986
South Platte	0,18	R^2=0,981	*	*	0,16	R^2=0,978

E2	k_{O2} (h^{-1})		$k_{O2+NaN3}$ (h^{-1})		k_{O2+Pro} (h^{-1})	
H_2OmQ	0,02	R^2=0,958				
Pinail	0,07	R^2=0,985	0,05	R^2=0,922	0,04	R^2=0,959
Suwannee	0,06	R^2=0,993	0,04	R^2=0,990	0,03	R^2=0,963
South Platte	0,14	R^2=0,973	*	*	0,11	R^2=0,937

* Not done

Conclusion

- Photodegradation of E1 and E2 is possible under natural sunlight
- Observation of DOM photosensibility
- Participation of singlet oxygen and hydroxyl radicals in the reaction
- Formation of a by-product

Future works

- Identification of the by-product (LC-MS)

- Development on the relationship between nature of DOM and its photoinductive properties (RMN ^{13}C, oxidation of DOM to the hydrophilic fraction)

- Study of by-product toxicity (osters)

Thank you